FERROMAGNETIC RESONANCE ABSORPTION IN COBALT SINGLE CRYSTALS

By

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Technical Report No. 187

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Abstract

Ferromagnetic resonance absorption of cobalt single crystals has been measured at ~24,200 Mc/s. The temperature range was restricted to 200°C (180°C to 300°C) due to the high anisotropy energy and the phase transition at 430°C. The anisotropy constants K_1' and K_2', the g-factor and the line width were determined at these temperatures using three single crystals of different crystallographical orientation.

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I

Introduction

A considerable number of measurements on ferromagnetic resonance absorption have been made since the discovery of the phenomenon by Griffiths in 1940.[1]   Most of the measurements, however, have been made on poly-crystals and, in cases of single crystals, materials cubic in structure. Except for the data reported in Griffiths' first paper there seems to have been no measurements made on cobalt which as a single crystal possesses a hexagonal lattice. The primary difficulty which confronts one in performing resonance measurements on cobalt is its high anisotropy energy. Thus a field of the order of 10,000 oersteds is required to assure saturation in polycrystalline cobalt. For this reason one cannot rely too much on the data presented by Griffiths who found resonance at 510 oersteds for $\lambda = 3$cm in polycrystalline cobalt. Although the saturation problem can be avoided by using a single crystal in the easy direction, the use of single crystals does not eliminate the difficulty presented by the high anisotropy energy as we shall see later.

Ferromagnetic resonance absorption was first treated theoretically by Kittel.[2] He showed that the phenomenon can be described by solving a classical equation of motion having the form,

$$\frac{dM_{xy}}{dt} = \gamma [\vec{M} \times \vec{H}_{eff.}]_{x,y} - \frac{M_{x,y}}{T_2} \tag{1a}$$

$$\frac{dM_z}{dt} = \gamma [\vec{M} \times \vec{H}_{eff.}]_z - (M_z - M_0)/T_1 \tag{1b}$$

Here $\gamma = g e/2mc$ and g is the so-called spectroscopic splitting factor. The dampening terms are the same as those adopted by Bloembergen[3] based on the form introduced by Bloch for nuclear magnetic resonance. The essential point in Kittel's discussion was to note that one had to take into consideration the field due to shape demagnetization and anisotropy besides the external field in the quantity $\vec{H}_{eff}$. In general one can write $\vec{H}_{eff}$ as,

$$\vec{H}_{eff} = \vec{H}_{ext} + \vec{H}_S + \vec{H}_a + \vec{H}_{exch} + \vec{H}_{st} \tag{2}$$

where $\vec{H}_{ext}$ is the external field, $\vec{H}_S$, the demagnetizing field, $\vec{H}_a$ the anisotropy field, $\vec{H}_{st}$ the effective field arising from strain and $\vec{H}_{exch}$ the effective field due to increase in exchange energy arising from an inhomogeneous distribution of magnetization. In our case $\vec{H}_{st}$ can be neglected. The quantity H_{ext} is proportional to $\nabla^2 M$ and hence zero if the sample is uniformly magnetized. It has been shown by Kittel and others to be negligible unless one goes down to very low temperatures where the skin depth becomes small. Although our sample was not of the shape that would ensure perfect homogeneity, the magnetization can be considered sufficiently homogeneous to render the quantity negligibly small as compared to the other terms when one considers the dimension ratios of the sample used and also the fact that only the middle portion of the sample facing the small aperture was subject to the r-f field. The equation of motion can now be solved by inserting

$$(H_{ext})_x = h e^{i\omega t}, \quad (H_{ext})_y = 0, \quad (H_{ext})_z = H_0$$

and by putting $M_{x,y} = m_{x,y} e^{i\omega t}$. Here h is the amplitude of the r-f magnetic field which is applied perpendicular to the external field H_0. The steady-state solutions are

$$m_x = \frac{\gamma^2 M_z \left\{ H_0 + \sum (N_y - N_z) M_z \right\} h}{\left[i\omega + (\frac{1}{T_2}) \right]^2 + \gamma^2 \left\{ H_0 + \sum (N_x - N_y) M_z \right\} \left\{ H_0 + \sum (N_y - N_z) M_z \right\}} \quad \ldots (3a)$$

$$m_y = \frac{\gamma^2 M_z (i\omega + \frac{1}{T_2}) h}{\left[i\omega + (\frac{1}{T_2}) \right]^2 + \gamma^2 \left\{ H_0 + \sum (N_x - N_y) M_z \right\} \left\{ H_0 + \sum (N_y - N_z) M_z \right\}} \quad \ldots (3b)$$

and the resonance condition is given by

$$\omega_0^2 = \gamma^2 \left\{ H_0 + \sum (N_x - N_y) M_0 \right\} \left\{ H_0 + \sum (N_y - N_z) M_0 \right\} + \frac{1}{T_2^2} \quad \ldots (4)$$

where we have put $M_z = M_0$, and

$$\sum (N_x - N_y) = (N_x^S - N_y^S) + (N_x^a - N_y^a) \quad \ldots (5a)$$

$$\sum (N_y - N_z) = (N_y^S - N_z^S) + (N_y^a - N_z^a) \quad \ldots (5b)$$

Here the effective fields due to shape demagnetization and anisotropy have been conveniently replaced by effective demagnetization factors, N_x^S, N_y^S, N_z^S and N_x^a, N_y^a, N_z^a, respectively. A general formula for deriving the effective fields and the effective demagnetization factors from the knowledge of the expression of energy has been derived by MacDonald.[4] In the case of cobalt, which has an hexagonal structure and is magnetically uniaxial, the easy direction of magnetization lying along the hexagonal axis, the anistropy energy can be expressed phenomenologically from symmetry considerations as follows,

$$E_a = K_1' \sin^2 \theta + K_2' \sin^4 \theta + \cdots , \quad (6)$$

where θ denotes the angle between the hexagonal axis and the direction of magnetization. As for fitting the magnetization curve, it has been shown that higher-order terms are not necessary. It is also known that in cobalt the hexagonal plane is isotropic within experimental errors. From Eq. (6) MacDonald obtains the following expression for the effective demagnetizing factors of anisotropy,

$$(N_x^a - N_z^a) = \frac{2}{M_o^2} \left[(K_1' + 2K_2')(\gamma_{zx'}^2 - \gamma_{xx'}^2) + 2K_2'(3\gamma_{xx'} - \gamma_{zx'}^2)\,\gamma_{zx'}^2 \right] \quad \dots \text{(7a)}$$

$$(N_y^a - N_z^a) = \frac{2}{M_o^2} \left[K_1' + 2K_2')(\gamma_{zx'}^2 - \gamma_{yx'}^2) + 2K_2'(3\gamma_{yx'} - \gamma_{zx'})^2\gamma_{zx'}^2 \right] \quad \dots \text{(7b)}$$

Here the primed coordinates refer to the coordinate system of the principal axes of the crystal and the unprimed ones to the coordinate system of the applied field. γ_{ij} is the direction cosine connecting the two coordinate systems. In the actual calculation, the expression for the anisotropy field is first derived in the coordinate system of the crystal. Secondly, the effective demagnetization factors are derived and then transformed to the system of the external field which is the actual laboratory coordinate system. Thus $N_x^a, \dots \dots$ are actually tensor quantities and should read N_{xx}^a, etc. The off-diagonal terms are not precisely zero but are known to be very small. To obtain a linear relation between the effective field and magnetization, i.e., $H_{eff}^a = \sum N^a M_o$, the quadratic terms of $m_{x,y}$ have been neglected. This is reasonable because $m_{x,y} \ll M_o$. From Eqs. (3a), (3b) and the relation for high-frequency susceptibility,

$$\mu - 1 = \mu_1 - 1 - i\mu_2 = 4\pi\chi = \frac{4\pi\,m_x}{h} \tag{8}$$

one obtains for the real and imaginary parts of the permeability the following expressions,

$$\mu_1 = \frac{4\pi\gamma^2 M_o\left\{H_o + \sum(N_y - N_z)M_o\right\}(\omega_o^2 - \omega^2)}{(-\omega^2 + \omega_o^2)^2 + \frac{4\omega^2}{T_2^2}} \tag{9a}$$

$$\mu_2 = \frac{4\pi\gamma^2 M_o\left\{H_o + (\sum(N_y - N_z)M_o)M_o\right\}\frac{2\omega}{T_2}}{(-\omega^2 + \omega_o^2)^2 + \frac{4\omega^2}{T_2^2}} \tag{9b}$$

Thus by measuring the frequency, the field for resonance, and the permeability, one can obtain values for the g-factor and the anisotropy constants from (4), (5a, b) and (7a, b) and the quantity T_2 from Eq. (9a) and (9b). In

the experiment to be described these quantities were derived for cobalt single crystal at a frequency of about 24,200 Mc/s (K-band).

II

Samples

Three cobalt single crystals cut in different orientations were kindly lent us through the courtesy of Professor Y. Shirakawa of the Tohoku University, Japan. All three were in the shape of thin rectangular slabs. The important dimensions are listed in Table I. Here θ denotes the angle between

Table I*				
Specimen	Width	Thickness	θ	Length of Span
[0001] axis	0.107"	0.0209"	11.2°	0.539"
[2ĪĪ2]	0.115"	0.0214"	53.8°	0.432"
[2ĪĪ0]	0.107"	0.0165"	80°	0.345"

the long axis of the rectangle and the hexagonal axis. In all our experiments the external field was applied along the long axis. Therefore θ coincides with the angle between the direction of magnetization and the hexagonal axis.

In performing resonance measurements with ferromagnetic con-ductors, one has to be very careful in the preparation of the surface as the skin depth is very small ($\sim 10^{-5}$ cm) at microwave frequencies. Thus very small surface strains will suffice to obscure the resonance completely. As has been shown by Kip and Arnold the resonance field will show practically no difference for different   orientation of single crystals if the surface is merely mechanically polished. It is necessary to electropolish the sample in order to remove the minute scratches and surface strains. The electro-polishing bath employed consisted of 90 per cent phosphoric acid and 10 per cent chromic acid. Good results were obtained when a current of 10 amp/cm^2

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*For further details, see K. Honda and Y. Shirakawa, Sci. Rep. Tohoku University. A, 1, 9. (1949).

was fed with the sample as the anode and a copper plate for the cathode.
It required about 3 to 4 minutes with the bath at room temperature in
order to attain a smooth, shiny surface. The polishing process was continued
until microscopic examination revealed no traces of scratches.

As already known, the only form that insures homogeneous magnetization
is an ellipsoid. In our case the form was a rectangular slab. However, it
was of such a dimension as to permit approximation as a prolate ellipsoid.
The demagnetization factors were calculated by the formula derived by
Osborn. The value for N_z^S was about 0.3. As the x- and y-components
only see a thickness of one skin depth, N_x^a can be taken as zero whereas
N_y^a can be taken as 4π.

III

Experimental Technique

The experimental technique was similar to the method employed by
Bloembergen:[3] The sample was placed at the end of a rectangular micro-
wave cavity which was excited by an r-f frequency field, and the power
reflected was measured as a function of the external static field. The sample
was placed in a position where the r-f electric field is zero and the r-f magnetic
field is directed perpendicular to the static field. A block diagram of the
apparatus is shown in Fig. 1. The power absorbed in the sample can be deter-
mined by measuring the unloaded Q, Q_u, and the external Q, Q_e of the cavity.
Q_u is related to Q_e by $Q_u = \beta Q_e$. β is the so-called coupling parameter and
for an undercoupled cavity is equal to $1/R$, where R is the voltage-standing-
wave ratio (VSWR). Owing to the shape and dimensions of our sample, we
were not able to adopt the conventional method of terminating the guide with
the sample or placing the sample inside the cavity. As seen in Section II,
the samples made available were in the form of thin rectangular slabs about
0.4 in. long, 0.1 in. wide and 0.02 in. thick (Table I). It was found neces-
sary to align the magnetic field along the long axis of the crystal. Other-
wise the demagnetizing factor would be either meaningless or prohibitively
large because of the large saturation magnetization of cobalt ($M \cong 1400$ gauss).
Thus if one attempts to apply the field normal to the surface the demagneti-
zing field would amount to about $4\pi M \cong 18,000$ gauss. This fact imposed
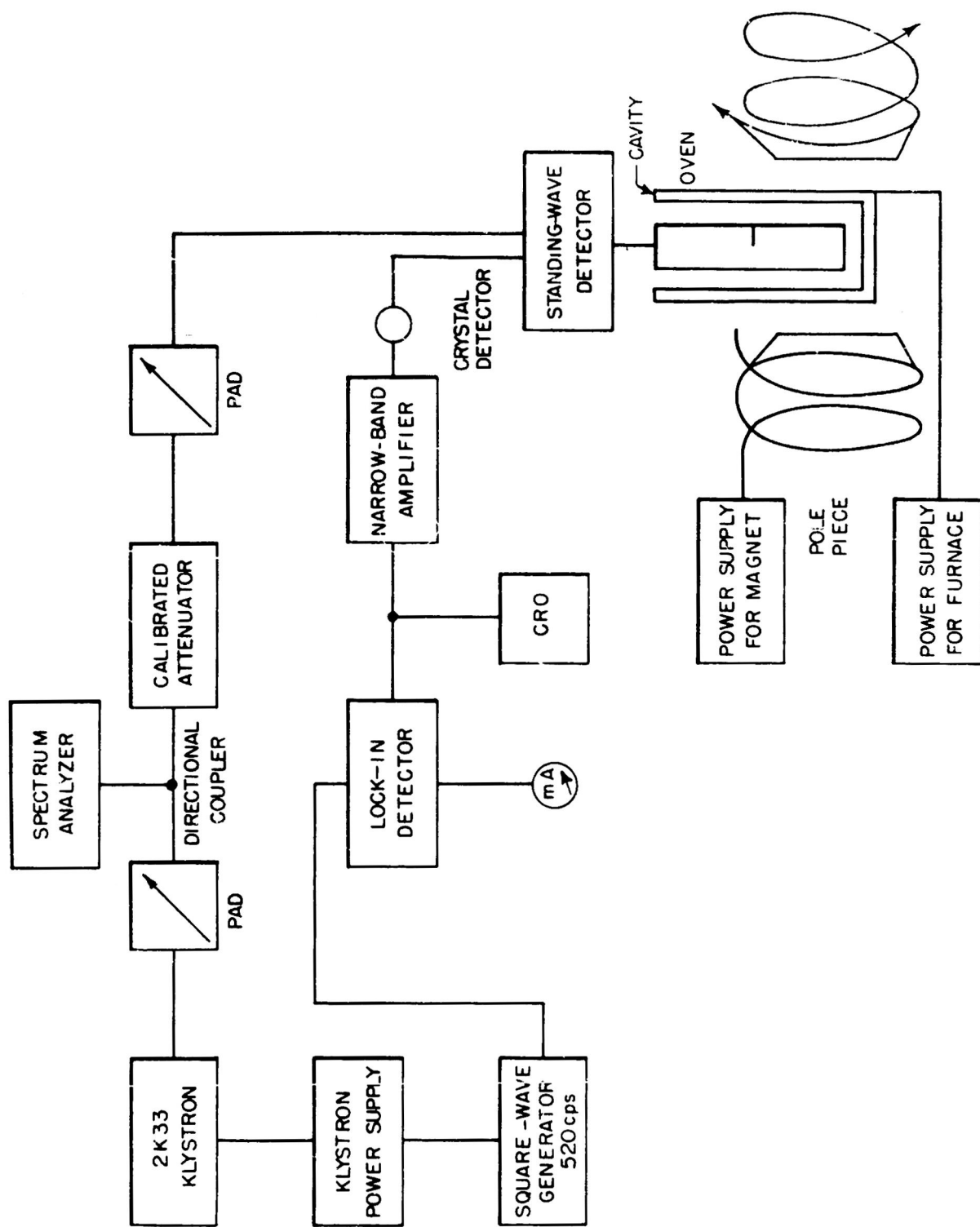
FIG. I BLOCK DIAGRAM OF APPARATUS

restrictions on the geometry of the sample relative to the cavity. Secondly,
the crystal could not be silver-soldered on to the end wall of the cavity
because of the existence of a phase transformation in cobalt at about $430^{\circ}C$.
Soft soldering was rejected because measurements at temperature over $300^{\circ}C$
were desired. Thus the cavity had to be constructed so that the crystal
could be mechanically mounted with the long axis parallel to the external
field.

Essentially three types of cavities were tested both at X-band and
K-band. (a) A groove large enough to insert the crystal was cut in a copper
block and the copper block as a whole was clamped on to the end of the guide.
(b) A copper plate with a slit large enough to insert the crystal was silver-
soldered on to the end of the guide. The sample was inserted in the slit and
clamped on from the outside. (c) A copper plate with a small circular
aperture in the middle was silver-soldered on to the end of the guide and
the sample clamped on over the hole from the outside. Of the three, the
first two, (a) and (b), were rejected for the following reasons. (a) At high
temperatures (over $150^{\circ}C$) the loss became prohibitively large. This is
probably due to the fact that the contact between the end wall and the guide
became bad and uneven due to thermal expansion. Furthermore, a hap-
hazard behaviour in the reflected power as the magnetic field was applied
was observed at higher temperatures. This is probably due to the fact that
when the magnetic field is applied a mechanical torque works on the crystal
if the field is not along the easy axis and if the sample is not perfectly
aligned parallel to the field. The torque, although small, can be large
enough to alter the electrical contact between the end wall and the guide,
and hence affect the Q of the cavity. (b) Losses were too large. The Q
in the X-band was already relatively low and in the K-band became too low
to be measured. Cavity (c) was constructed with the object of eliminating
all possible spurious effects resulting from changes in electrical contact
of the end wall plus sample and guide, and also to cut down the losses to a
minimum. As for the electrical contact, further precautions were taken by
inserting a thin mica sheet between the end wall and the sample, which was
clamped on from the outside so that the middle portion of the sample covered
the aperture. Results were favorable, the unloaded Q being about 2500 at

room temperature and about 1800 at about 300°C. The only disadvantage
of this type of cavity was that the available area of the sample was re-
stricted, thus diminishing the change in reflected power due to resonance
effects. The change in some cases was indeed small but, at the very
smallest, well over the noise level of the lock-in detector output. Thus
cavity (c) was adopted for all the measurements. Outside of the end wall,
which shorted a section of the rectangular guide, the cavity was coupled
through an asymmetrical iris and excited in the E_{102} mode. (The length
of the cavity was therefore one guide-wave-length long (Fig. 2).)

The microwave power at about 24,200 Mc/s was generated by 2K33
klystron. The power was square-wave-modulated at 520 cps and fed
through paddings and a calibrated attenuator into the cavity. The re-
flected power was passed through a directional coupler and detected by
a crystal detector. The detected signal was then passed through a 520 cps
narrow-band amplifier and into the lock-in detector. The VSWR was
measured by a slotted-line standing-wave detector. A portion of the
microwave power was fed into a spectrum-analyzer in order to measure
the frequency. The procedure of measurement was as follows; First, the un-
loaded Q was determined at zero field by measuring the VSWR as a function
of frequency. Next, the external field was increased in appropriate steps
and the VSWR measured at each field. Actually the VSWR was measured
at one or two fields only. For the rest of the points only the reflected
power was measured and R determined by the relation,

$$\frac{P_r}{P_i} = \frac{(1-R)^2}{(1+R)^2}$$,

where P_r in the reflected power and P_i the incident power. This convenient
procedure could be used because P_i is kept constant throughout the measure-
ment. In all our measurements the cavity was undercoupled to the extent
that P_r was about 15 to 20 per cent of P_i. This corresponds to a VSWR
of about 2.

The static field was supplied by a conventional electromagnet. The
field was determined by a flip coil which was calibrated at one point with
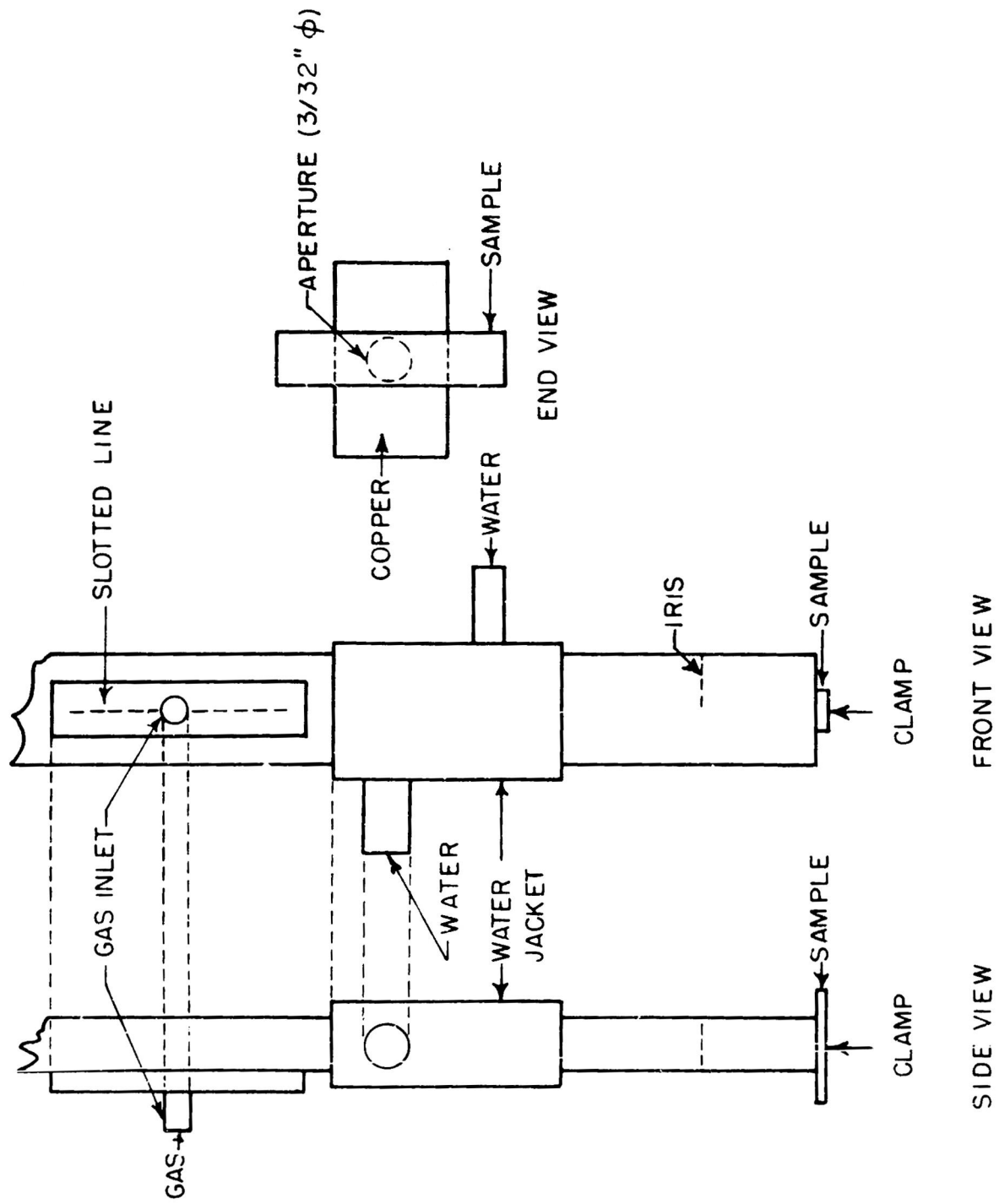a proton magnetic resonance. The gap between the pole pieces was about

FIG. 2 DESCRIPTION OF CAVITY

3 inches. A field of about 7500 oersteds was attained with a current of about 10 amp. at 200 volts.

As we shall see later. it was found necessary to make all the measurements at elevated temperatures (200°C to 400°C). In order to prevent oxidation of the cavity and sample at these temperatures a gas consisting of 80 per cent nitrogen, 20 per cent hydrogen was introduced into the cavity. A mica sheet was inserted in one section of the guide to prevent the gas from escaping. A section of the guide was also water-cooled so that the heat would not extend to the whole apparatus. The outside of the cavity was merely flushed by the gas. This was sufficient to suppress the oxidation to an appreciable extent.

From the values of Q_u and R determined by the procedure described above, one can calculate the high-frequency permeability in the following manner: In our arrangement, only a small portion of the sample restricted by a circular aperture 3/32 in. in diameter is exposed to the microwave field. Thus we may assume that the introduction of the sample causes only a small perturbation. This is to say that the distortion of the field configuration in the cavity due to the introduction of the sample is negligibly small. Then one can employ the perturbation method developed by Bethe and Schwinger and others to derive the relation,

$$\frac{\delta f}{f} + j\delta\left(\frac{1}{2Q_u}\right) = \frac{\delta W}{W} \qquad \qquad \cdots \quad (10)$$

Here f is the resonant frequency of the cavity and W the total stored energy of the cavity; δf and δW are the changes in these quantities due to the introduction of the sample. If the field configurations in the cavity are known, W and δW can be calculated in terms of μ. Unfortunately it was difficult to determine the field configuration in the present set-up where the sample is clamped on from outside of the cavity. Accordingly one cannot hope to determine the absolute of μ with exactness. However, the shape of the resonance curve (μ versus H) should be fairly good as $\mu \sim \Delta Q$ and the relative values of μ can be determined. It should be noted here that the μ we are speaking of is the part of the complex permeability that determines the losses in the cavity. In a non-conducting material this is just the

imaginary part, μ_2. In a ferromagnetic metal, however, the smallness
of the skin depth at very high frequencies alters the situation and the
losses are now determined by a so-called effective permeability

$$\mu_R = (\mu_1^2 + \mu_2^2)^{1/2} + \mu_2.^6$$

Table II

Temp. °C	$K_1' \times 10^5$ ergs/cm^3	$K_2' \times 10^5$ ergs/cm^3	$(K_1 + K_2) \times 10^5$ ergs/cm^3	g
180	4.57	10.8	15.3	2.65
200	2.92	9.16	12.1	2.50
220	.93	7.58	8.51	2.39
240	- 1.05	5.98	4.93	2.30
260	- 3.69	5.53	1.84	2.27
280	- 6.20	4.87	- 1.33	2.23
300	- 8.82	4.55	- 4.27	2.22
320	-11.3	4.49	- 6.77	2.22
340	-13.7	4.20	- 9.50	2.23
360	-15.7	4.11	- 11.6	2.24
380	-17.6	4.05	-13.6	2.28

IV

Results

The anisotropy constant of hexagonal cobalt is known to be about
6×10^6 ergs/cm^3 at room temperature, an order of magnitude larger
than that for iron and nickel. The effective field of anisotropy at room
temperature turns out to be about $\dfrac{2K_1}{M_0} \simeq 7000$ oe and $\dfrac{2K_2}{M_0} \simeq 600$ oe, respectively.

Owing to this unusually high anisotropy field it requires a frequency of
30,000 Mc/s at zero applied field in order to observe resonance when the
external field is applied parallel to the easy axis. Therefore in order to
observe resonance at K-band (24,400 Mc/s) and at external fields high
enough to warrant saturation it was necessary to go to higher temperatures
where the anisotropy constants become sufficiently small. With the field
applied along the easy axis, the resonance was first observed at about 150°C
with an external field of about 1000 oersteds. For the difficult direction the
resonance field at lower temperatures was much higher than the maximum
field our magnet could produce. Thus the measurements at K-band were
restricted to a relatively small temperature range of about 200°, the lower
limit imposed by the high anisotropy field and the upper limit by the ir-
reversible phase transformation which occur at about 420°C. The range,
however, covers the region where the switch in the axis of easy magnetization
from the hexagonal axis to the hexagonal plane takes place.

The temperature dependence of the field of resonance H_o for the three
crystals are plotted in Fig. 3. One can see qualitatively from this figure
how the shift in the magnetic axis takes place. Bearing in mind the fact
that the crystal nearest to the easy axis should resonate at the lowest field
it is apparent that the shift does not take place abruptly, but gradually over
a temperature range of about 100°, starting from about 220°C and ending at
about 320°C, and that at about 270°C the 45° direction becomes the easy axis.
The points of intersection in this figure cannot be taken too seriously due to
the fact that the shape demagnetization factors for the three crystals are
different. There is also about 1% difference in frequency. It is necessary
to derive more significant quantities such as the anisotropy constants in
order to look into the situation on a quantitative basis.

(a) Anisotropy constants

From the experimental values of H_o and frequency, and from the
knowledge of the direction of the crystal relative to the principal axes,
we obtain at each temperature three independent equations of the form Eq. (4).
The unknown quantities are the g-factor and the two anisotropy constants K_1'
and K_2'. Therefore the equations can be solved for K_1' and K_2' if we assume
that the g-factor is isotropic. The assumption, although plausible, may be

open to question as the cobalt does not possess cubic symmetry.
It is unfortunate that this point could not be checked directly as
it would require a fourth independent equation if the g-factor is
assumed anisotropic. Further discussions concerning this point
will be made later. With the assumption of isotropic g-factor, the
simultaneous equations which are quadratic in K_1', and K_2' were
solved by a convenient method of successive approximation. The
results obtained for the anisotropy constants are shown in Table II
and Fig. 4. The values for saturation magnetization were taken
from recent measurements on cobalt single xtals made by Myers
and Sucksmith.[7] It can be seen that K_1' is still rapidly changing
whereas K_2' already shows tendency of levelling off. It is noted that
we are still far below the Curie temperature which lies at about
$1000^{\circ}C$. On the other hand we are quite near the temperature at
which cobalt transforms from a hexagonal close-packed structure
to a face-centered cubic structure (polycrystalline) which lies at
about $430^{\circ}C$. Sucksmith and Myers have shown that for a single
crystal the change in saturation magnetization takes place discon-
tinuously at the transformation point. Presumably the anisotropy
constants act similarly so it is not surprising that K_1' shows no in-
dication of a minimum. The quantity $K_1' + K_2'$, which is the differ-
ence in magnetic energy between the hexagonal axis and the hexagonal
plane, has also been plotted. The dotted lines represent the results
on $K_1' + K_2'$ calculated by McKeehan using the data on magnetization
curves measured by Honda and Masumoto.[8] His results scatter
somewhat on the scale used but one can see that it is roughly parallel
to our results with a difference of about $1 \times 10^5 \, erg/cm^3$. The anisot-
ropy constants have also been calculated by Bozorth[9] using the same
data. The general trend is again similar but the actual values are diffi-
cult to compare. Especially noticeable is the difference in the temper-
ature at which K_1' changes sign. Bozorth's curve reads about $200^{\circ}C$
whereas our curve reads $228^{\circ}C$. This temperature is particularly
significant due to the fact that the magnetic axis starts to shift
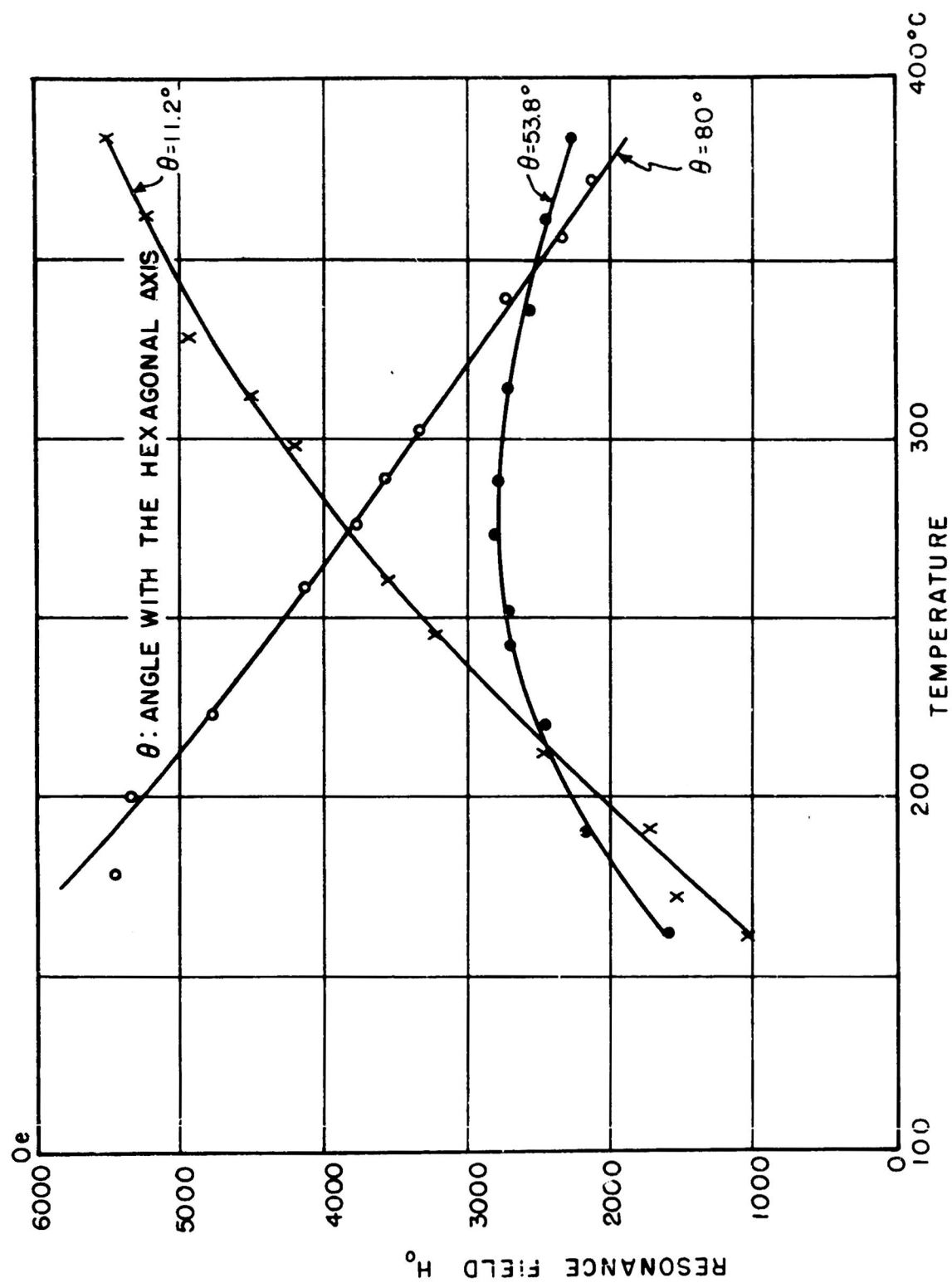
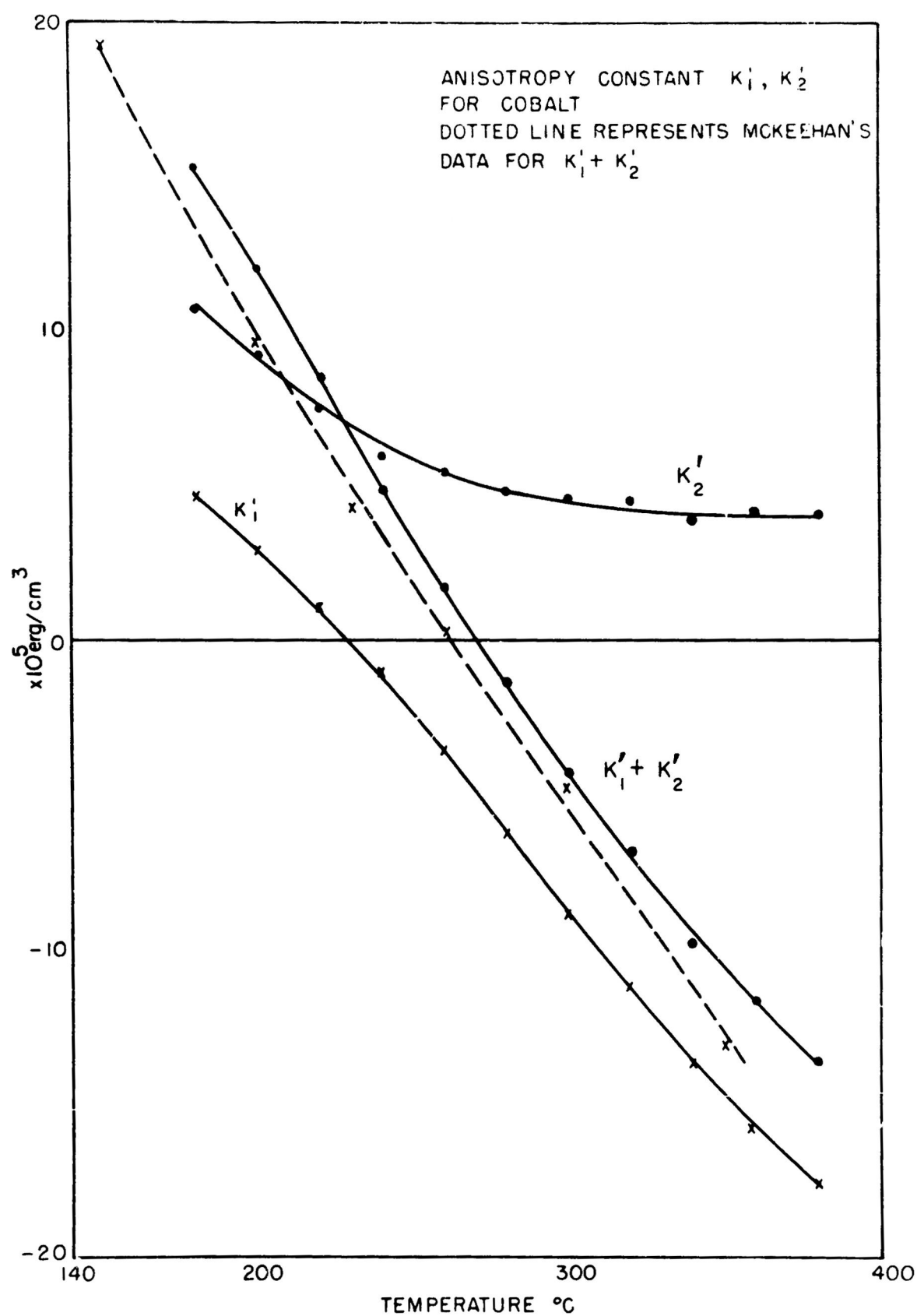FIG. 3   RESONANCE FIELD H₀ VERSUS TEMPERATURE
IN COBALT SINGLE CRYSTALS

FIG.4 ANISOTROPY CONSTANTS K_1', K_2'

directions at this point. This can be seen in the following manner. The direction of easy magnetization is determined from the condition of minimum anisotropy energy; namely,

$$\frac{\partial E_a}{\partial \theta} = 0 \; , \quad \frac{\partial^2 E_a}{\partial \theta^2} > 0 \qquad ,$$

where E_a has the form as expressed in Eq. (6). Carrying out the differentiation, one finds,

$$\frac{\partial E_a}{\partial \theta} = K_1' \sin\theta \cos\theta + 2K_2' \sin^3\theta \cos\theta = 0 \qquad \ldots (12a)$$

$$\frac{\partial^2 E_a}{\partial \theta^2} = K_1 (\cos^2\theta - \sin^2\theta) + 2K_2' (3\sin^2\theta \cos^2\theta - \sin^4\theta) > 0 \quad \ldots (12b)$$

or

$$\theta = 0 \qquad \text{when} \qquad K_1' > 0$$

$$\theta = \pi/2 \qquad \text{when} \qquad K_1' + 2K_2' < 0$$

In other words the easy direction will be parallel to the hexagonal axis as long as K_1' remains positive and in the hexagonal plane when $-K_1'$ becomes larger than $2K_2'$. In between these values the easy direction will not lie along the principal axes and will be determined by the solution of Eq. (6) with $\sin\theta \neq 0$ and $\cos\theta \neq 0$, i.e.,

$$\sin\theta = \sqrt{-\frac{K_1'}{2K_2'}} \qquad\qquad (13)$$

The temperature range at which the magnetic axis takes intermediate directions can be determined from the known values of K_1' and K_2'. A plot of $K_1' + 2K_2'$ was made and it was found that $K_1' + 2K_2' = 0$ corresponded to $303^\circ C$. Thus the magnetic axis starts to deviate from the hexagonal axis at $228^\circ C$ and ends in the hexagonal plane at $303^\circ C$. The direction of easy magnetization in between these temperatures was calculated

from Eq. (7) and is shown in Fig. 5.

Although the origin of ferromagnetic anisotropy is generally believed to lie in the interplay between spin-orbit coupling and orbital valence, the theory itself is still far from satisfactory. Apart from computational difficulties, a basic defect is that the theories do not predict a correct temperature variation. Thus it is, unfortunately, not possible to compare our results in detail with theory. Vonsovosky,[10] however, has computed the temperature dependence of K_1' based on the Bloch-Gentile model[11] and has shown that under certain conditions it is possible for the sign to change. What he essentially shows is that at very high temperatures K_1' should be negative whereas at absolute zero it can be positive if certain restrictions are imposed on the relative magnitude of terms. The reason why these conditions may be allowed is not clear. Perhaps all one can say at the present is that the switch in the magnetic axis is determined by the temperature dependence of K_1'. It has been pointed out by Bloch and Gentile and Van Vleck[12] that the dipole-dipole coupling of pure magnetic origin yields much too small a value for K_1'. However, Van Vleck has shown that the spin-orbit coupling and the orbital valence produce an interaction which can be expressed as dipolar in nature. He called this a "pseudo-dipolar" coupling. In cubic crystals the first-order effect of pseudo-dipolar coupling is zero due to symmetry considerations. However, for hexagonal crystals the first-order effect does not drop out and this is what determines K_1'. In an ideally close-packed hexagonal crystal the nearest neighbors would not contribute to K_1', but the further neighbor would. To sum up, it may be said that the shift in the easy direction from the hexagonal axis to the hexagonal plane arises from the temperature dependence of the first-order effect of dipolar coupling whereas the second-order effect tends to suppress the switch-over and spreads it out over a finite temperature range.

The accuracy of our results on K_1' and K_2' can be estimated as follows; As described previously, K_1' and K_2' are evaluated by assuming the g-factor to be isotropic and eliminating from Eq. (4) the variable γ. With three independent equations one then ends up with two independent equations which, after expanding the brackets, can be expressed as
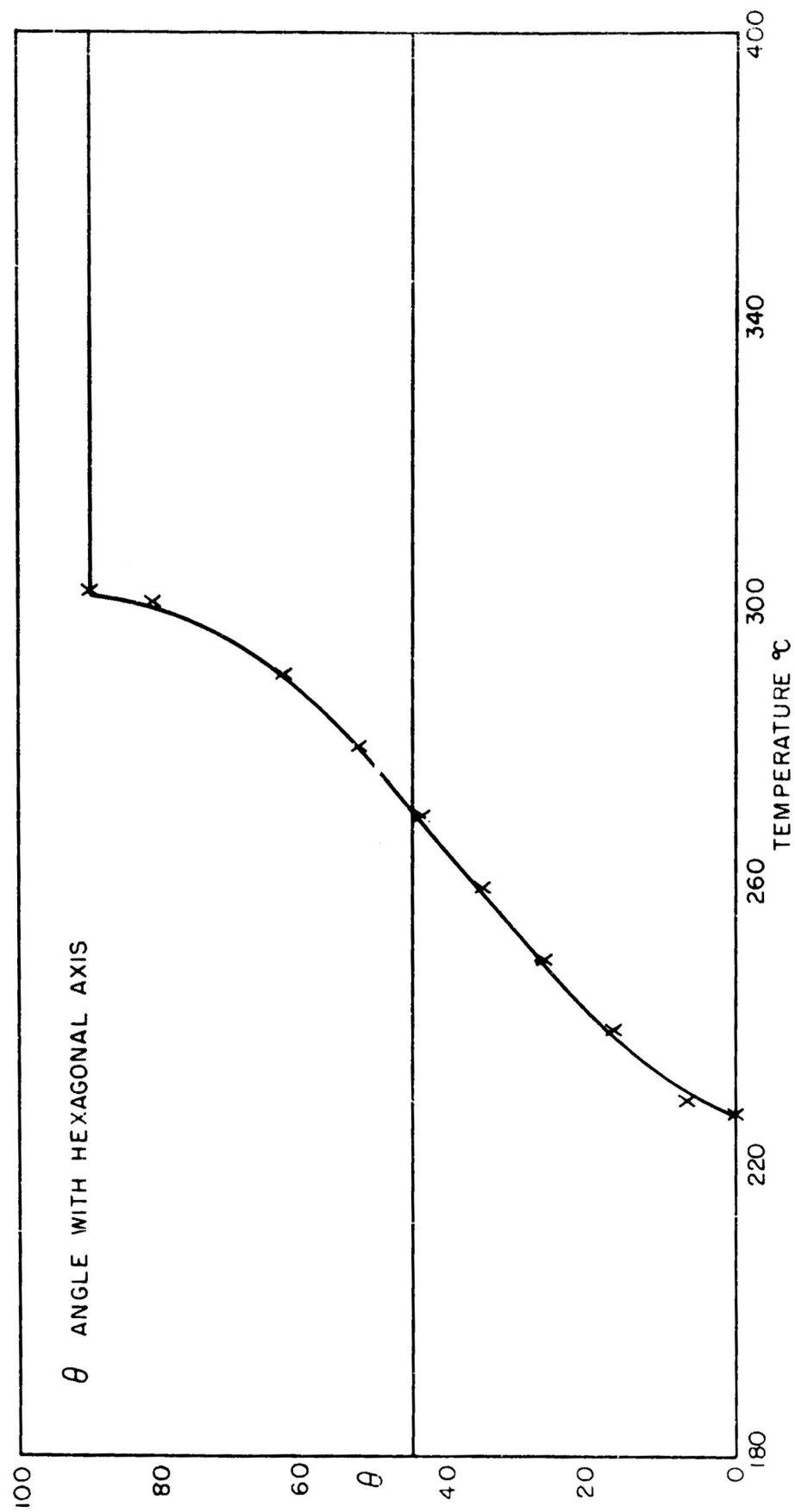
θ ANGLE WITH HEXAGONAL AXIS

FIG. 5 DIRECTION OF AXIS OF EASY MAGNETIZATION VERSUS TEMPERATURE

$$u + x_1 K_1' + x_2 K_2' + (\text{terms quadratic in } K_1', K_2') = 0$$

$$u' + x_1' K_1' + x_2 K_2' + (\text{terms quadratic in } K_1', K_2') = 0$$

Actual computations show that a good approximation can be obtained with the quadratic terms neglected. The main errors arise from uncertainties in u, x_1, x_2, etc. In addition, there is also the so-called inherent error which is due to the interaction of errors in solving the simultaneous equations. now the constants u, x_1, x_2, etc. involve the resonance field H_o saturation magnetization M_o, shape demagnetization factor N, and the directional cosines of the angle between the hexagonal axis and the orientation of the crystal. Considering the fact that the results on M_o obtained by Myers and Sucksmith were in good agreement with the results of Honda and Masumoto and that the values of M_o obtained by various authors on different crystals vary only by 0.3% at the most, M_o is probably good within 1 to 2% at the most. The error in H_o was not more than 3%. N is estimated to be good within 10%. The angle θ is probably not more than 2° off. With these errors, one finds that the worst combination of errors results in an over-all error of about 6% in the anisotropy constants. The probable error will presumably be smaller.

(b) g-factor

The g-factor was obtained by inserting the evaluated anisotropy constants back into the resonance equation. The results show a steady decrease in the g-value from 2.6 at 180^oC to 2.2 at about 240^oC, at which point it tends to level off, and stay constant up to 380^oC within experimental error (Fig. 6, Table II). This behavior is in contrast to previous experiments on ferromagnetic resonance which show that the g-value is practically independent of temperature. Thus it is rather striking to see a change in g with temperature amounting to about 20 per cent in a comparatively small temperature range and so far away from the Curie point. We shall first look into the sources of error which enter into the determination of g. By far the largest source comes from M_o and H_o which combine to give the leading term $H_o B_o$ in the resonance equation. Allowing a 1 per cent error for the frequency ν, 2 per cent for M_o, and

3 per cent for H_o it turns out that $\frac{\delta g}{g} = 2\%$. The remaining terms contribute
at the most 1 per cent. The g-factor is very insensitive to the shape de-
magnetizing factor and the anisotropy energy. For instance, a 30 per cent
error in N or K_1', K_2' will result in a error less than 0.5 per cent in g. Thus,
altogether the g-factor should be good to about 3 per cent. On the other hand,
the change in g amounts to about 20 per cent and it would require a 20 per cent
error in H_o and B_o in order to account for the change as an error. It also is
noted that the error must be a systematic one appearing at low temperatures
if one wishes to make the g temperature-independent. Apart from the fact
that an error of 20 per cent or more in H_o or B_o is highly improbable, it is
difficult to see how a systematic error could enter. Furthermore, one notes
that the saturation magnetization changes by only 3 per cent from 180° to
400'C and a change of more than 3 per cent in M_o at the low-temperature
side would conflict with the temperature variation of M_o. Therefore, con-
siderations of errors do not alter the essential feature of the anomaly. How-
ever, there are still reasons to believe that the anomaly may be spurious.
This is due to the fact that in solving the simultaneous equations we conven-
iently assumed g to be isotropic. The g-factor, however, is in general a
tensor quantity and there is no assurance that this assumption is correct.
More explicitly, what we have assumed is that $g\perp = g \parallel$ where $g\perp$ and $g \parallel$
are respectively the g-factors perpendicular and parallel to the hexagonal
axis. Now the deviation ϵ of g from the pure spin value of 2 is determined
by the strength of the spin-orbit coupling and the splitting of the degenerate
levels in the crystalline field of the solid, i.e., $\epsilon \sim \frac{\lambda}{\Delta}$ where λ is the spin-
orbit coupling constant and Δ the energy difference between the split levels.
Although λ may be fairly isotropic, a slight deviation from cubic symmetry
may cause considerable anisotropy in the level splitting Δ. Whether this
can explain the anomaly itself is still open to question because one still has
to explain why the change takes place primarily on the lower temperature
side. All this will have to be determined by future experiments at lower
temperatures and in more than three orientations. It is probably premature
to speculate any further until all the ambiguity is eliminated.

(c) Line Width

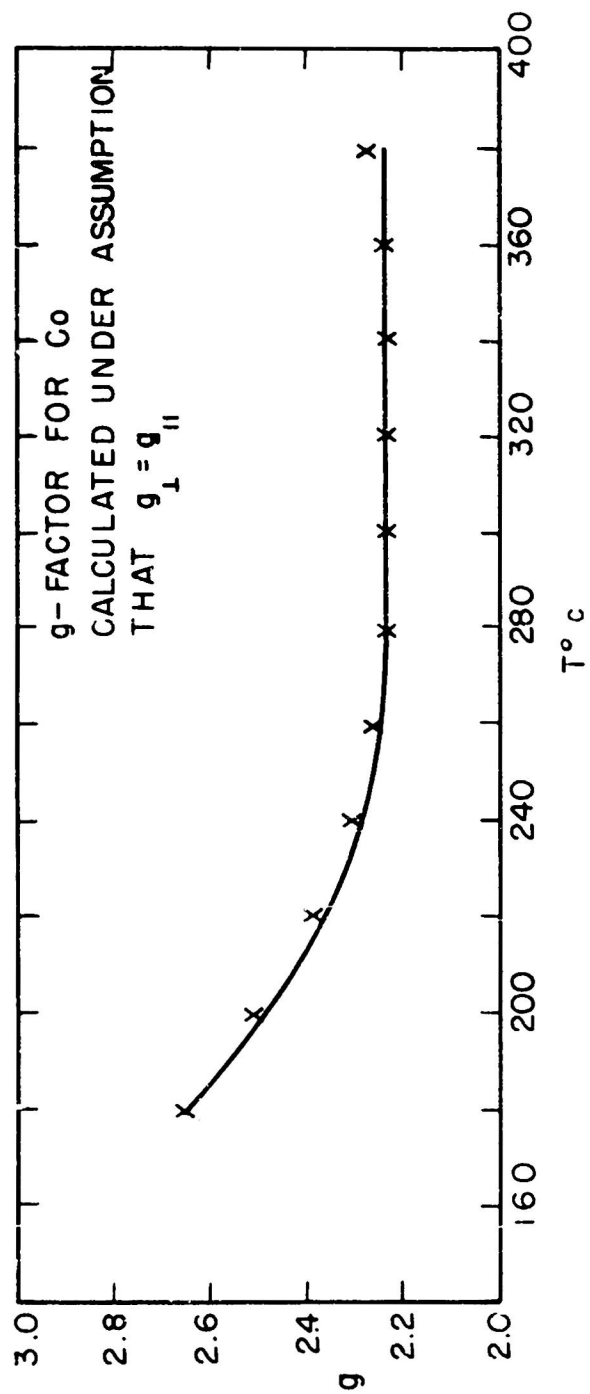   As previously discussed (Sec. III), we were not able to determine the

g-FACTOR FOR Co
CALCULATED UNDER ASSUMPTION
THAT $g_\perp = g_{\parallel}$

FIG. 6   g--FACTOR VERSUS TEMPERATURE

absolute value of μ_R. However, relative values of μ_R should suffice in the determination of the line width which depends on the shape of the resonance curve. Owing to the relatively small signal change arising primarily from the smallness of the effective sample value, the measurements on the line width cannot be relied on too much. Moreover, the fact that the sample was not of the form that would rigorously assure homogeneity in magnetization and that there did exist a small grain of different orientation in each crystal may well contribute to the line width although they are negligible as far as the shift in the central resonance frequency is concerned. Therefore detailed information, such as the difference in line width for different crystallographic orientations and the temperature dependency, was all within the limits of experimental error.

The line-widths for all three crystals were of the order of a few hundred oersteds. This corresponds to a relaxation time (T_2) of the order of 10^{-9} sec, a value normally yielded by ferromagnetic substances.

IV

Conclusion

The results obtained may be summarized as follows: Although the measurements had to be restricted to a relatively narrow temperature range, the interesting phenomenon of the reversal of sign in K_1' already known from magnetization curve measurements has been definitely confirmed. Unfortunately the present state of theory does not allow detailed discussion of the phenomenon. The fact that resonance experiment is a more sensitive method of determining the anisotropy may permit one to confirm whether terms of higher order than $\sin^4\theta$ are really negligible or not. This would require another crystal of different orientation. It is highly desirable at this stage to perform the same experiments on a disk-shaped sample. This would enable one to get as many independent equations as necessary and therefore will not only determine whether or not higher-order terms in the anisotropy energy are necessary but also will eliminate ambiguity in the assumption of the isotropic g-factor. It is also desirable to extend the temperature range to much lower temperatures. This would require measurements at millimeter waves. A disk-shaped sample now becomes almost

mandatory, since at low temperatures one would have to work fairly close to the easy direction in order to insure saturation.

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